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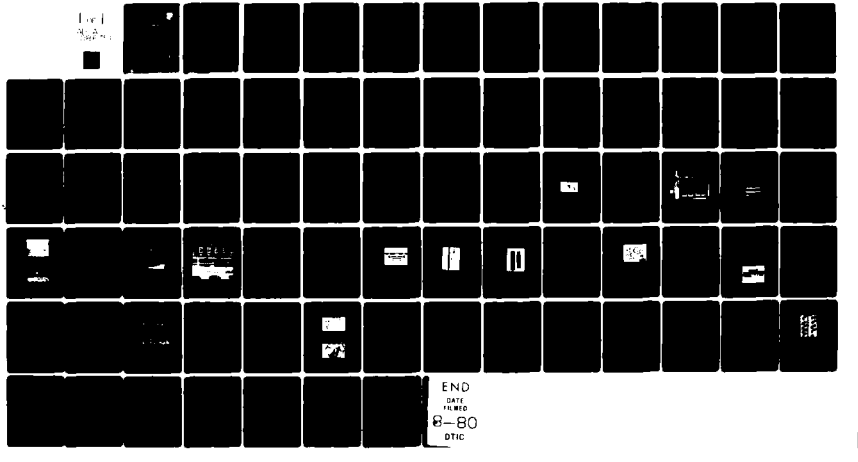

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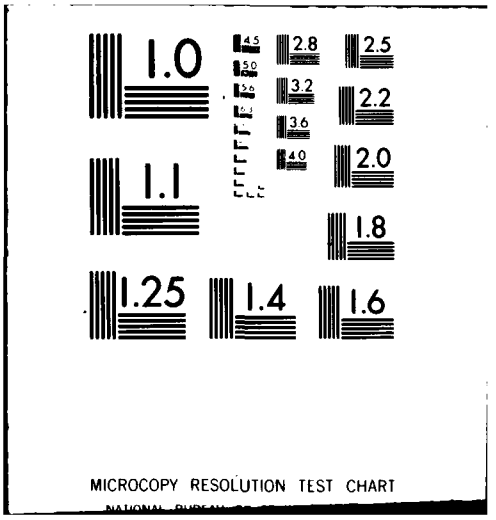
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Final Technical Report
March 1980

THE GROWTH OF BERLINITE ($AlPO_4$) SINGLE CRYSTALS

Litton Systems, Inc.

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Single crystals of the berlinite mineral phase of anhydrous aluminum orthophosphate have been grown for possible surface acoustic wave applications. The desired piezoelectric form of $AlPO_4$ is the α-phase which is stable from 130°C to 580°C. A seeded hydrothermal growth technique was used. Nutrient was prepared by heating hydrated alumina and phosphoric acid in a sealed silver liner from 140°C to 200°C at a rate of 5°C/day and a 15°C temperature gradient. Because

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$AlPO_4$ has retrograde solubility, the nutrient was placed in a silver mesh basket in the upper, cooler portion of the liner with the seeds situated in the lower, hotter portion. A 20% free area baffle separated the two regions.

Two basic techniques were used for the growth runs. The constant temperature method with a 10°C gradient produced rates of 23-25 mils/day. The rates could be varied significantly depending on such parameters as growth temperature, gradient, nutrient basket mesh size, seed orientation and baffle design. The second technique used increasing temperature at a rate of 5°C/day over the range of 140-200°C to obtain average growth rates of 22-32 mils/day. Seed orientation for most runs was (0001) plates.

New growth of $AlPO_4$ for the most part was clear and of fair quality. Crystals had what appeared to be high angle grain boundaries and crevice flaws which originate from the seed plate.

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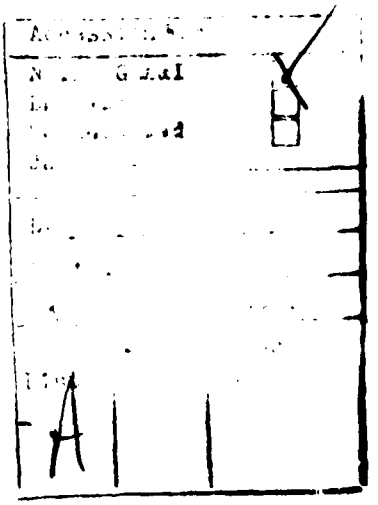

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SUMMARY

This project was initiated to investigate the single crystal growth of the berlinite mineral phase of anhydrous aluminum orthophosphate. The desired piezoelectric form of $AlPO_4$ is the α-phase which is stable from 130° to 580°C and is a direct analogy to quartz. Preparation of pure α-$AlPO_4$ by melting was impossible and a solution method was necessary. Since the vapor pressure of water rises rapidly with temperature, a closed hydrothermal system was used. In a seeded hydrothermal growth process, the starting materials (nutrient) of appropriate purity and particle size were dissolved by the solvent and transported to a portion of the closed system where the seeds were positioned. Due to the thermal gradient along the system, the previously saturated solution becomes supersaturated in the seed region resulting in growth, if the growth parameters are suitable.

Aluminum phosphate was insoluble in water at ordinary pressure and temperature and therefore appropriate conditions and solvents had to be found. Phosphoric acid was used as the solvent. $AlPO_4$ was more soluble in concentrated rather than dilute phosphoric acid and as the temperature increased, it was less soluble in the acid (retrograde solubility). The normal autoclave internal arrangement of seeds, nutrient, temperature gradient and general operation had to be altered because of the retrograde solubility. Due to the low pH and corrosiveness of the acid solution, an inert material such as silver had to be used to contain the 6 M phosphoric

acid. Silver cylinders (liners) 1.5 inches O.D. and 14 inches long were developed for the material preparation and growth experiments. The liners were heated in 3 inch O.D. by 1.5 inch I.D. steel autoclaves equipped with bandheaters and thermocouples.

Nutrient preparation for seeded growth runs was best produced by heating hydrated alumina and phosphoric acid in a sealed 3 inch O.D. silver liner from 140° to 200°C at a rate of 5°/day and a 15° temperature gradient. The product was small $AlPO_4$ crystals which were sieved to yield 1-4 mm size nutrient. In order to best utilize the thermal convections of the system, the seeded growth runs had the nutrient positioned in the upper portion of the liner in a silver mesh basket with the seeds in the bottom section. A 20% free area baffle separated the two regions.

Two basic techniques were used for the growth runs. The constant temperature method with a 10°C gradient produced rates of 23-25 mils/day. The rates could be varied significantly depending on such parameters as growth temperature, gradient, nutrient basket mesh size, seed orientation, and baffle design. The growth rates were for short duration runs of about a week, but decreased significantly for long runs.

The second technique used increasing temperature at a rate of about 5°C/day over the range of 140-200°C to obtain average growth rates of 22-32 mils/day. This rate was maintained for the run duration. Seed orientation for most of the runs was (0001) plates. Several experiments used rhombohedral seeds but the rates were only 2-4 mils/day.

New growth of $AlPO_4$ for the most part was clear and of fair quality. Two problems, however were observed. The crystals had what appeared to be high angle grain boundaries which were traced to the original seed plate. The quality of the starting seed determined the overall quality of the grown crystals. A second feature observed was deep pits or crevices found on the (0001) face of the crystals. Seed etching prior to growth and various seed orientations were studied but crystal quality was not affected.

The problem of $AlPO_4$ quality does not have a simple solution. A more detailed study is necessary to ascertain the exact nature of the quality defects and their relationship to the growth process.

PREFACE

This Final Technical Report describes experimental work performed under Contract No. F 19628-77-C-0213 from 1 July 1977 to 30 September 1979. The contract was titled objectively as "Growth of Berlinite ($AlPO_4$) Crystals". The project was initiated by and performed for the Rome Air Development Center of the Air Force Systems Command. Dr. Alton Armington was assigned as the contracting officer designated technical monitor.

All experimental work described in the report was performed in the laboratories of the Airtron Division, Litton Systems, Inc., 200 East Hanover Avenue, Morris Plains, New Jersey 07950. The general direction of the program was supervised by Dr. Roger F. Belt. The principal investigator and project engineer on all crystal growth was Dr. Larry E. Drafall. Mr. Karl Jensen and Ramesh Khurana prepared all materials.

EVALUATION

This report is the final report on the contract. It covers research done on the Growth of Berlinite from 1 July 1977 to 30 September 1979. The objective of the research was to investigate the hydrothermal growth of Berlinite ($AlPO_4$) to determine the optimum growth conditions for large high quality crystals. Over thirty hydrothermal growth runs were made both for the preparation of starting material and crystal growth. Crystals over a centimeter size were provided but the quality of the crystals was not satisfactory for device application. Samples are presently undergoing evaluation at RADC/ES. This work could have applications both to TPO R5D and RO 2.3.

The work is of value because it provides basic knowledge and techniques for the crystal growth of Berlinite. An in-depth understanding of the Acoustic Surface Wave Properties of this material is essential for their use in frequency and timing applications.

Alton F. Armington

ALTON F. ARMINGTON
Project Engineer

1.0 INTRODUCTION

Berlinite is the natural mineral form of anhydrous aluminum phosphate, $AlPO_4$. The single crystal is isostructural with crystalline quartz and therefore a piezoelectric material of some importance. The properties[1] of $AlPO_4$ were recognized and measured as early as 1949. In order to obtain reliable measurements, good quality crystals were required in a fairly large size. The early history of growing $AlPO_4$ and two satisfactory methods for obtaining research size crystals have been reported.[2] Nearly simultaneous studies were performed in Germany.[3] The early conclusions from piezoelectric tests were that $AlPO_4$ had a lower Q, a lower coupling coefficient, and lower modulus than quartz. Furthermore the temperature coefficient was larger than that in quartz and there was little opportunity of finding a zero temperature cut similar to the AT cut of quartz. After this investigation the importance of $AlPO_4$ diminished.

In 1965 a renewed interest in many old and several new piezoelectric compounds was created by discoveries and possible applications of surface accoustic waves (SAW). The materials position[4] in this attractive device field has been reviewed as recently as 1976. However, even though such now common crystals as quartz, $LiNbO_3$, TeO_2, $Bi_{12}GeO_{20}$ were studied in detail, there is no mention or discussion of $AlPO_4$. By way of summary, certain information is essential for SAW theory. Among the most needed data are surface wave velocities with and without

thin conductors, electromechanical power flow angles, basic piezoelectric properties, temperature coefficients of velocity, or changes in delay times with temperature. One of the first indications that $AlPO_4$ may bear a much closer scrutiny and property measurement was given by work of Barsch and Spear.[5] These workers performed measurements on crystals grown at the U.S. Army Signal Corps and they found that $AlPO_4$ had a larger electromechanical coupling factor k than quartz did for certain cuts. More measurements of fully characterized crystals are essential on temperature effects. Some preliminary data on thermal properties are already published.[6] The whole matter of temperature compensation in piezoelectric materials has been examined more closely[7] and rapid advances may be forthcoming in understanding the phenomena.

In spite of advances in theoretical work, it is mainly the availability of crystals of $AlPO_4$ that has limited unambiguous measurements. The growth of any single crystal is usually a tedious process and the method is primarily dictated by fundamental physical properties. For $AlPO_4$ some of these properties will be discussed in Section 2. Usually if a crystal is stable at its melting point, the easiest and direct way to get large crystals is by the Czochralski method of pulling from the melt. For $AlPO_4$ the desired piezoelectric form is part of the phase which is stable only up to about 580°C where it undergoes a transformation (similar to quartz) to a new phase. Obviously it is

impossible to prepare pure α-$AlPO_4$ by melting and other methods must be sought. At the lower temperature end, the formation of anhydrous $AlPO_4$ is also complicated. Only above 130°C does the $\alpha AlPO_4$ crystallize from water solutions. Thus the major stability region extends from 130°C to 580°C and a solution method of growth is indicated in direct analogy to quartz. This is the conclusion arrived at earlier by other workers.[2,3]

Even though a solution method is necessary, the vapor pressure of water rises rapidly with temperature and unless a closed system is designed, the solution composition will change continuously and drastically. Thus essentially we must work in a closed hydrothermal system to grow α-$AlPO_4$ even though the pressures and temperatures are not as high as in the growth of quartz. A wealth of experience from quartz hydrothermal growth is available[8,9] and most of this can be applied directly to α-$AlPO_4$. However two important differences must be noted. First in addition to water, α-$AlPO_4$ must be grown from an acid solution which is usually H_3PO_4, while quartz is always grown from basic solution. Ordinarily this presents no difficulties except for autoclave or liner (container) materials. Finally another important difference is the retrograde solubility of $AlPO_4$ in H_3PO_4. Retrograde solubility contributes a difference in autoclave internal arrangement of seeds, nutrient, temperature gradient and general operation. These will be explained more fully in other sections of this report. For the present it is sufficient to note that in the temperature range of 250-300°C,

the solubilities of α-$AlPO_4$ and quartz are roughly equivalent.

2.0 EXPERIMENTAL

2.1 Physical Data of $AlPO_4$

The crystal structure of berlinite ($AlPO_4$) was determined[10] to be similar to quartz with the unit cell of $\underline{a}$ = 4.93 Å where $\underline{c}$ is double that of quartz. The space group is $P3_121$ or $P3_231$ with 3 formula units per unit cell. The berlinite structure is derived from the quartz structure by replacing the Si ions with Al and P ions which double the unit cell along $\underline{c}$.

The morphology of hydrothermally grown crystals showed doubly terminated hexagonal pyramids composed of both major and minor rhombohedral faces almost equally developed. The interfacial angles of the crystal forms $(10\bar{1}0)$, $(10\bar{1}1)$, $(01\bar{1}1)$ and $(10\bar{1}2)$ of $AlPO_4$ are compared to quartz in Table I.

The thermal expansion of $AlPO_4$ was determined[6] from 293°K to 950°K by the x-ray powder diffraction method through the transition at about 857°K. Figure 1 gives the lattice parameters of berlinite versus temperature. The six single crystal elastic constants of $AlPO_4$ have also been measured between 80°K and 298°K by the ultrasonic pulse superposition method.[6] Temperature compensated cuts with zero temperature coefficient of the resonance frequency at 25°C are found with orientations similar to those for AT and BT cuts in α-quartz, but with a larger electromechanical coupling factor.[6] Table I compares some additional physical properties of $AlPO_4$ and SiO_2.

Table I

Comparison of $AlPO_4$ and SiO_2 Properties

	Trigonal quartz (W.R. Wyckoff)[10]	$AlPO_4$ (Huttenlocher)[15]	Berlinite (Strunz)[21]	Berlinite (Chang&Barsch)[6]	$AlPO_4$ NBS, Perloff[22]
Density (g/cm^3)	2.65	2.560	2.64	2.620	2.618 (calc)
Mohs Hardness	7	6	5-7		
Unit Cell Parameters (Å)					
a_o	4.90	4.93	4.92	4.943 00.001	4.942
c_o	5.39	2x5.47	2x5.45	2x5.487 0.005	2x5.49
$c_o:a_o$	1.10	2x1.11	2x1.11	2x1.11	
Refractive Indices					
E_D	1.553	1.530	1.529		1.530
W_D	1.544	1.524	1.523		1.524
$E_D - W_D$	0.009	0.006	0.005		0.006

	Trigonal quartz	$AlPO_4$ (Jahn&Kordes)	$AlPO_4$ (Stanley)
Interfacial Angles			
$(10\bar{1}0)$ $(20\bar{2}1)$	21° 29'		
$(10\bar{1}0)$ $(10\bar{1}1)$		21° 16'	
$(10\bar{1}0)$ $(10\bar{1}1)$	38° 13'		
$(10\bar{1}0$ $(10\bar{1}2)$		37° 36'	
Piezoelectric modulus d_{11} (X cut) coul/newton	2.3×10^{-12}		1.4×10^{-12}
Dielectric Constant	4.34		≈5
Coupling Coefficient	0.10		0.051

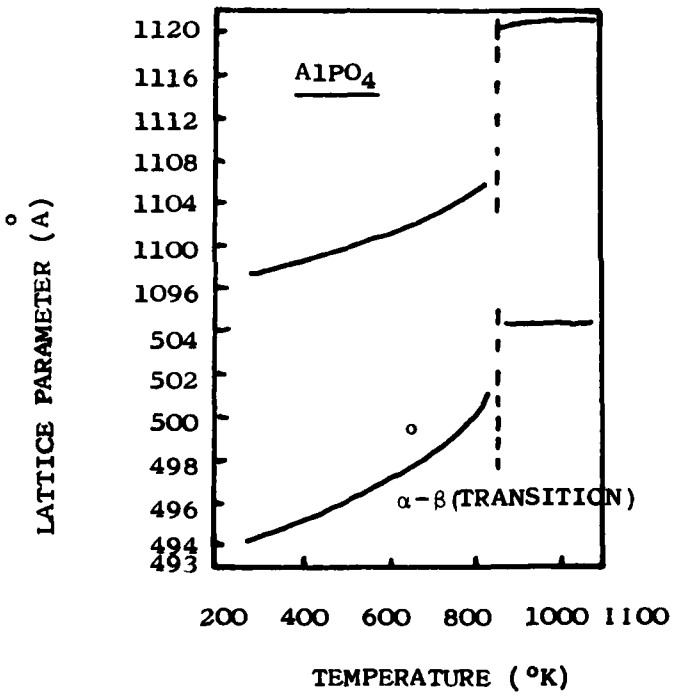


Fig.1 Lattice parameters of berlinite versus temperature

2.2 Phase Stability

Aluminum orthophosphate has the analogs of quartz, tridymite and cristobalite along with the minor alpha-beta transitions.[1] Mooney[11] determined that orthorhombic aluminum orthophosphate had the space group $C222_1$ with $4(AlPO_4)$ per unit cell and not the small primitive tetragonal cell used for comparison with low cristobalite. Beck[1] studied the crystallographic relation to those of silica and should be consulted for a more detailed discussion.

The inversion in berlinite has been determined to 6 Kbar by differential thermal analysis in a hydrostatic apparatus. From near 584°C at 1 Kbar the transition temperature rises linearly with pressure at the rate of 26.0 ± 0.5 deg/Kbar.[12] Values for the transition obtained by other workers are 586 ± 2°C. (Beck, 1949).[1] 581 ± 1°C. (Troccoz et al., 1967)[13] and 580°C. (Florke and Lachenmayr, 1962).[14] Figure 2 shows the variation with pressure of the high-low berlinite inversion temperatures. From the figure, one can see that hydrothermal growth of $AlPO_4$ is well below the temperatures and pressures of the tranisition and was not a factor in growth.

2.3 Materials Preparation

Phosphate chemistry is very complex and certain precautions must be taken during preparation to obtain the desired phase. Many different stoichiometries of aluminum phosphate and its hydrates are possible as shown in Figure 3. Preparation

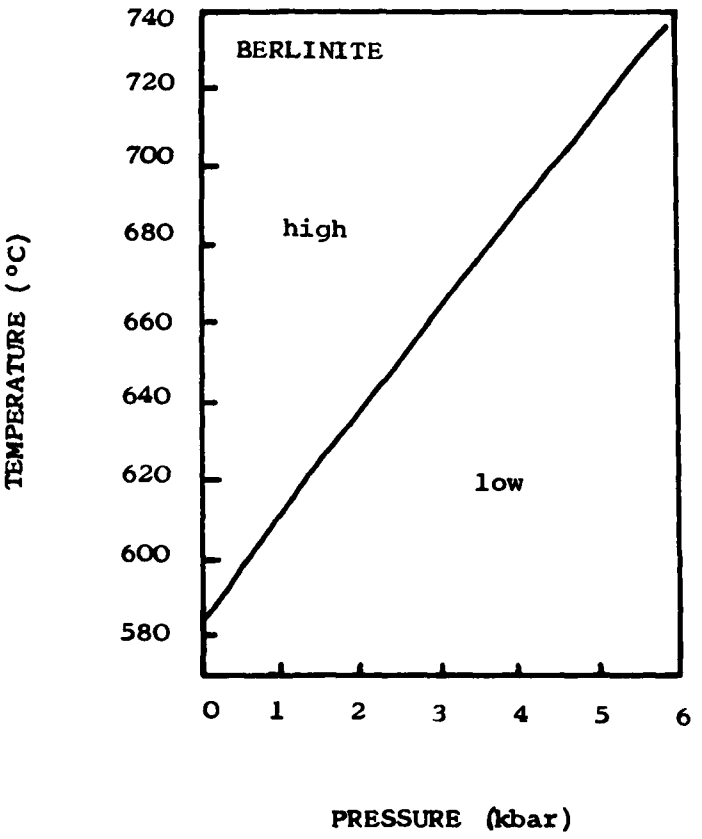


Fig.2 Variation with pressure of the high-low berlinite inversion temperatures.

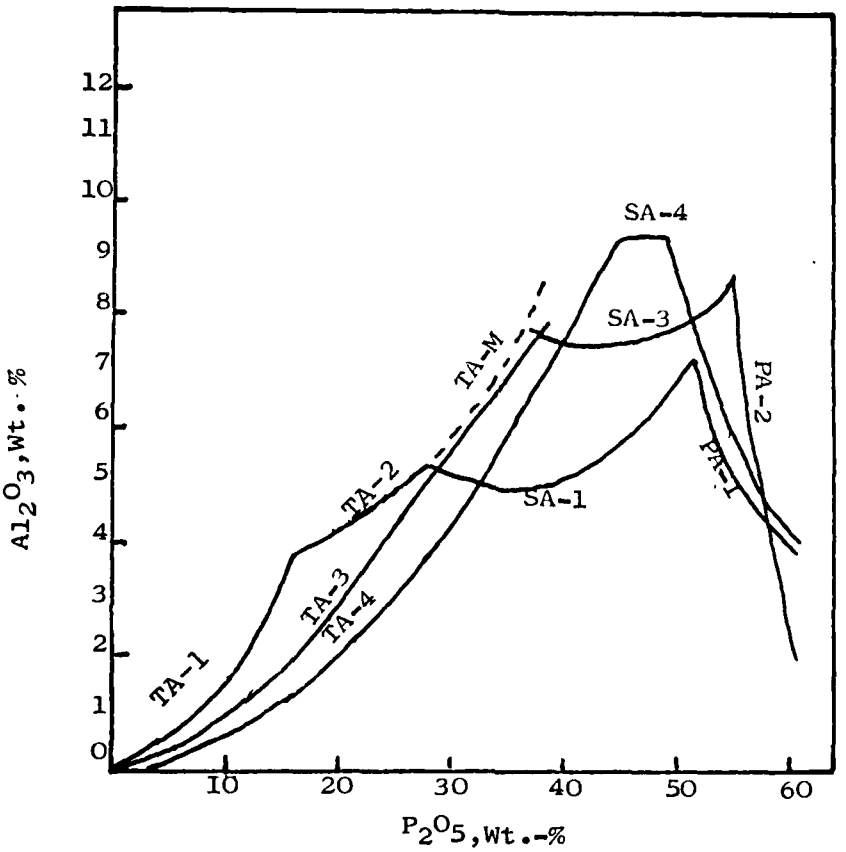


Figure 3 System Al_2O_3-P_2O_5-H_2O

[From R.F. Jameson and J.E. Salmon, J. Chem. Soc., 1954]

25°C TA-1 = $AlPO_4 \cdot 3.5H_2O$ SA-1 = $Al_2(HPO_4) \cdot 3H_2O$

TA-2 = $AlPO_4 \cdot 2H_2O$ PA-1 = $Al(H_2PO_4)3 \cdot 1.5H_2O$

[From J.C. Brosheer et al., J. Am. Chem. Soc. 76, 5951 (1954)]

25°C TA-M = Metastable region from $AlPO_4 \cdot xH_2O$

40°C TA-3 = $AlPO_4 \cdot xH_2O$

SA-3 = $AlH(PO_4)_2 \cdot H_2O$

PA-2 = $Al(H_2PO_4)_3$

75°C TA-4 = $AlPO_4 \cdot xH_2O$

SA-4 = $AlH(PO_4)_2 \cdot 3H_2O$

PA-2 = $Al(H_2PO_4)_3$

[From V.N. Sveshnikova, Russian J. Inorg. Chem. (English trans.) 5, 227 (1960]

can be accomplished by several different methods and the purity of the product varies largely with the particular preparation technique. The following paragraphs describe various procedures used previously and considers those methods which will produce the highest purity $AlPO_4$.

For determining the structures of aluminum phosphate, Huttenlocher[15] prepared the material by precipitation from ammonium alum using ammonium phosphate after the addition of sodium acetate. He also employed a reaction between concentrated orthophosphoric and concentrated sodium aluminate to obtain aluminum phosphate. A white crystalline product was obtained after heating in a closed pipe for several hours at 250°C. Sodium aluminate can be purchased or prepared as follows:

$$Al + NaOH + H_2O \rightarrow NaAlO_2 + \frac{3}{2} H_2 \quad (1)$$

The aluminum can be in the form of a metal or any soluble salt but upon hydrolysis a gel usually forms which can incorporate impurities. The $NaAlO_2$ is then reacted with the phophoric acid.

$$NaAlO_2 + 2H_3PO_4 \rightarrow AlPO_4 + NaH_2PO_4 + 2H_2O \quad (2)$$

Stanley and others have utilized the reaction between sodium aluminate and orthophosphoric acid. There are two difficulties with this reaction even though $AlPO_4$ can be crystallized from solution. First the $NaAlO_2$ is not of high purity and second, some NaH_2PO_4 obviously appears in the solution and product. It is not clear what effect it has on hydrothermal growth.

Aluminum phosphate has been prepared at NBS by the direct dissolution of Al metal in phosphoric acid according to the following reaction:

$$Al + H_3PO_4 \rightarrow AlPO_4 + \frac{3}{2} H_2 \quad (3)$$

The reagents were placed in a Morey-type hydrothermal bomb and heated. This technique would be most satisfactory in respect to purity since high purity aluminum metal (99.99%) is available and incorporation of impurities from the aluminum salt needed in the other techniques is eliminated. Kolb and Laudise[16] have used $AlPO_4$ of an unknown purity but variable stoichiometry and phase. Thus the compounds were merely a convenient source of aluminum and phosphorous. Jahn and Kordes[3] have described several other experiments which employed various aluminum salts in a reaction with H_3PO_4. Among the most attractive are the hydrated aluminas of various origins and composition.

Our initial work attempted the $NaAlO_2$ approach with the following modifications. High purity aluminum metal (Table II) was reacted with sodium hydroxide according to the following equation.[3]

$$Al + NaOH + H_2O \rightarrow NaAlO_2 + \frac{3}{2} H_2 \quad (4)$$

We have carried out this process at room temperature but normally the product appears as a gel which preferably must be dried prior to use. The gel was tried directly but problems arise on handling, weighing, autoclave loading, and composition. Finally, even though some $AlPO_4$ was obtained, the crystallized product was not of the best quality. Our preliminary crystallization was performed in silver tubes which were heated in Tem-Pres type autoclaves. The rate of heating was fixed at 5-10°C per day after a rapid heating to 130°C. At the end of 2-3 weeks the autoclaves were cooled

Table II

Analysis of Aluminum Metal

Aluminum (metal) 'ANALAR'	
Al	Atomic wt. 26.98
Wire 0.76 mm (0.03 inch)	
Description: A bright, silver-gray metal	
Minimum assay	99.9% Al
Maximum Limits of impurities	
Acid-insoluble matter	0.005%
Nitrogen compounds (N)	0.001%
Silicon (Si)	0.005%
Copper (Cu)	**0.005%**
Iron (Fe)	**0.004%**
Manganese (Mn)	**0.002%**

rapidly to room temperature to prevent further dissolution of any $AlPO_4$.

We have developed a better procedure by using hydrated alumina or $Al(OH)_3$ in a reaction with H_3PO_4 according to equation (5).

$$Al(OH)_3 + H_3PO_4 \rightarrow AlPO_4 + 3H_2O \quad (5)$$

In this method the hydrated alumina is weighed and enough H_3PO_4 is added to react according to (5) and producing a final solution which is 6 M in H_3PO_4. Thus the only product is $AlPO_4$ in H_3PO_4 solution. To facilitate the initial dissolving, the solution can be warmed carefully to about 90-100°C. Care should be taken to avoid extensive loss of water or conversion to higher phosphoric acids. Some of the properties of aluminas we have found to be suitable are tabulated in Table III. The analysis of the orthophosphoric acid is given in Table IV.

One other materials preparation technique was used for $AlPO_4$. Aluminum isopropylate was melted and poured into warm deionized water to evolve alcohol. The solution was mixed thoroughly and then evaporated with the residue dissolved in phosphoric acid. The saturated solution was then sealed in a silver liner following the usual procedure for nutrient preparation.

2.4 Solubility

Aluminum phosphate is insoluble in water at ordinary pressure and temperature and therefore appropriate conditions and solvents had to be found. Phosphoric acid has been used as a

TABLE III

Properties of Hydrated Aluminas

Property	C-33	C-331	710
Al_2O_3 (%)	65.0	65.0	64.7
SiO_2 (%)	0.008	0.01	0.04
Fe_2O_3 (%)	0.002	0.006	0.01
Na_2O_3 (%)	0.15	0.15	0.45
Moisture (110°-%)	0.04	0.40	0.30
Loose density (lb/ft^3)	60-70	44	8-14
Pack density (lb/ft^3)	75-85	77	16-28
Spec. Gravity	2.42	2.42	2.40
On 100 mesh (%)	0-1	-	-
On 200 mesh (%)	5-10	-	-
On 325 mesh (%)	30-60	-	.04
Through 325 (%)	40-70	99	99.9+
Index refract.	1.57	1.57	1.57

Note 1. Theoretical analysis is 64.35% Al_2O_3 and 34.65% H_2O.

Table IV

Analysis of 85% H_3PO_4

(2.37 liters)

H_3PO_4 F.W. 98.00

MEETS A. C. S. SPECIFICATIONS

Maximum Limits of Impurities

Arsenic (As)	0.0001%
Chloride (Cl)	0.0003%
Heavy Metals (as Pb)	0.001 %
Insoluble Matter, Calcium Magnesium, and Ammonium Hydroxide Precipitate	0.005%
Iron (Fe)	0.003%
Manganese (Mn)	0.00005%
Nitrate (NO_3)	0.0005%
Potassium (K)	0.005%
Reducing Substances	To Pass Test
Sodium (Na)	0.025%
Sulfate (SO_4)	0.003%
Volatile Acids (as $HC_2H_3O_2$)	0.001%
ASSAY (H_3PO_4)	Min. 85.0%
Color	ALPHA
SP. GR.	1.7

solvent for $AlPO_4$ crystals because growth occurs most readily from solutions in which the solute is fairly soluble. Aluminum phosphate is much more soluble in concentrated rather than dilute phosphoric acid and as the temperature increases, it is less soluble in the acid (retrograde solubility). The solubility of $AlPO_4$ in 6M H_3PO_4 has been determined by Stanley only in the range of 145-245°C (Figure 4). An Arrhenius plot of this data, assuming a rate controlled reaction, is given in Figure 5 where suitable extrapolation can be made to 300°C. In the range of 290-360°C the data of Jahn and Kordes are useful and plotted in Figure 6. There appears to be a region where retrograde solubility ceases and normal increasing solubility begins. This solubility change was studied recently [17] as a function of temperature (150° to 550°C), pressure (up to 1400 bars) and solvent concentration (5M to 12M).

2.5 Purity

The chemical purity of aluminum phosphate is quite variable due to the relatively large number of stable phases possible. Commercially available chemicals usually are supplied in several purities. Previous growth of aluminum phosphate crystals[2] indicated that C.P. sodium aluminate and phosphoric acid conforming to ACS requirements produced a brown precipitate at first attributed to the action of phosphoric acid on the glass container and the steel bomb, but later was traced to the sodium aluminate reagent. $AlPO_4$ dissolved in ACS grade phosphoric acid produced excellent crystals. Certified reagent

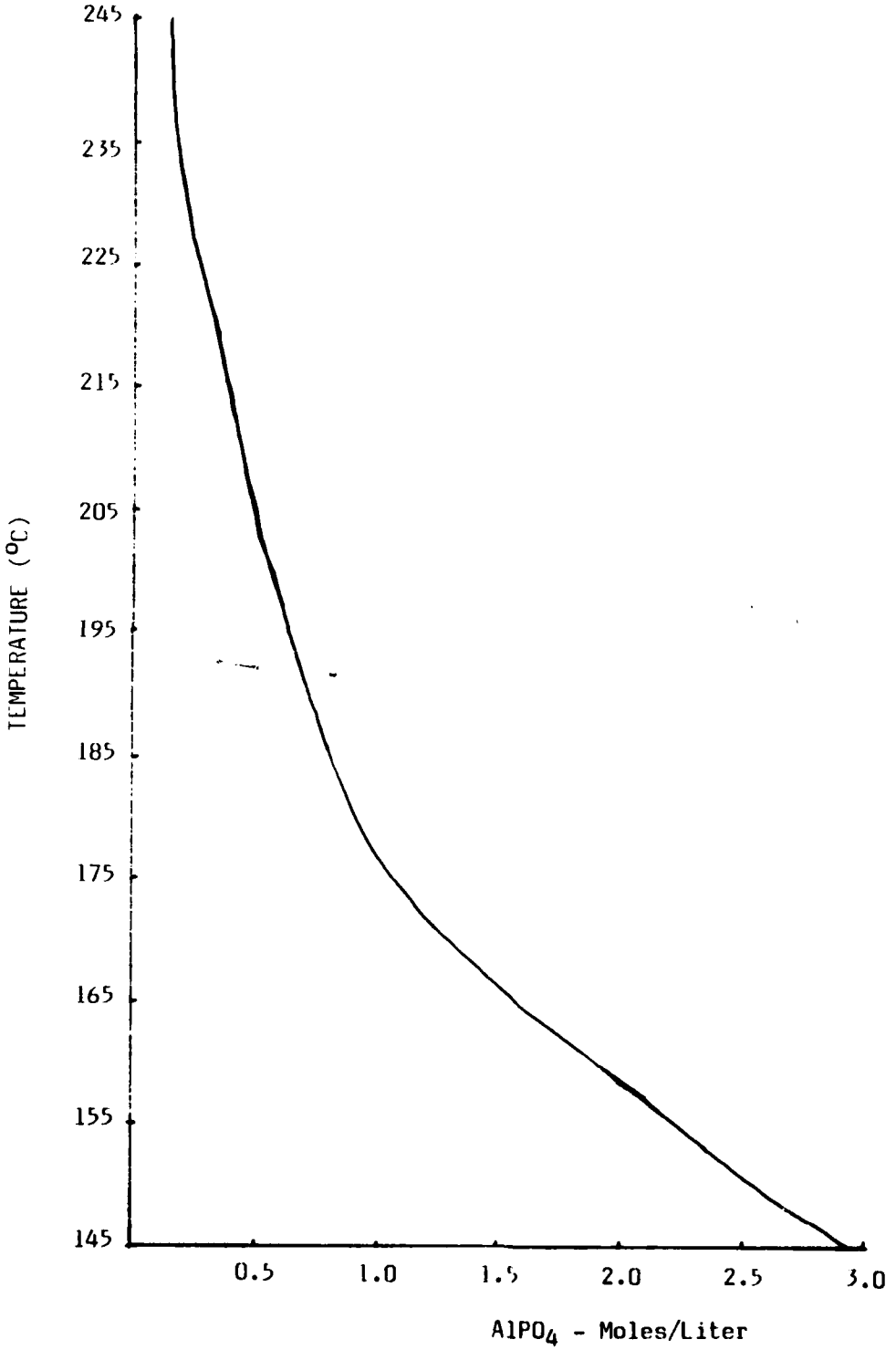


Figure 4. Solubility Curve for $AlPO_4$ in 6.1 M Phosphoric Acid.[2]

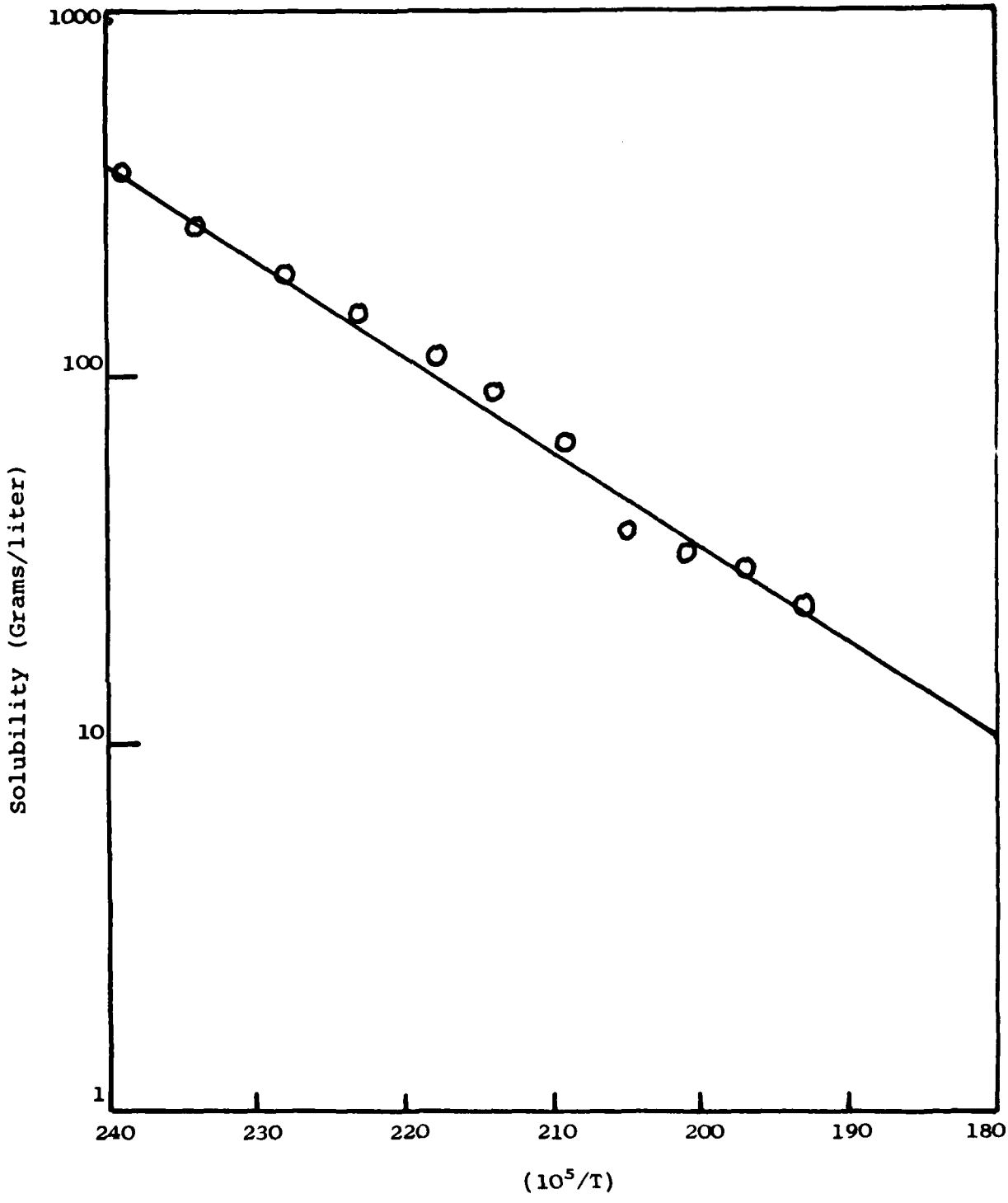


Figure 5 Arrhenius Plot of Stanleys' [2] Solubility Data on $AlPO_4$

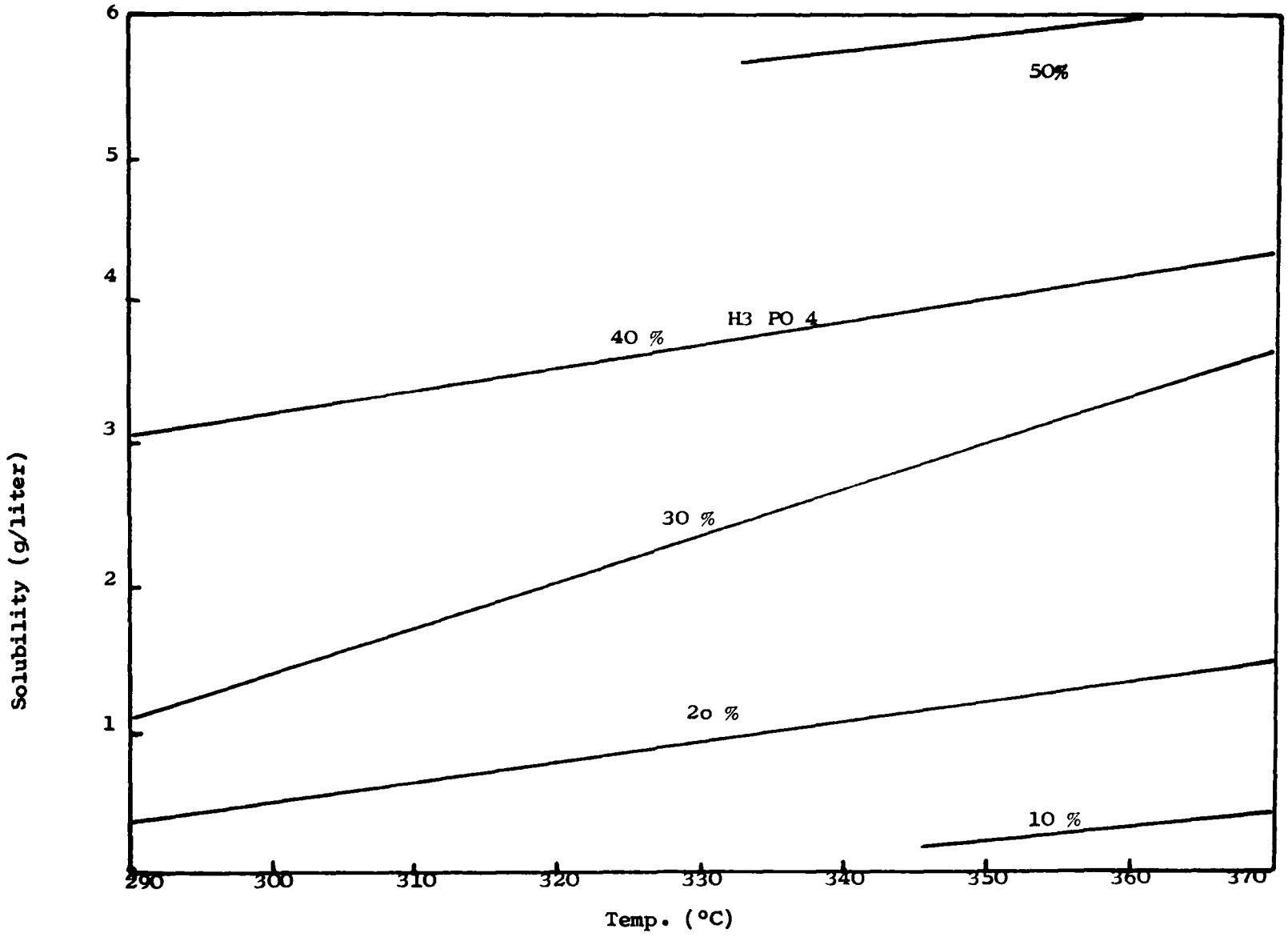


Figure 6 Solubility of $ALPO_4$ in H_3PO_4 Solutions[3]

grade hydrated aluminum orthophosphate ($AlPO_4.2H_2O$) is commercially available. Anyhdrous aluminum orthophosphate purchased from a vendor was actually identified as aluminum metaphosphate [$Al(PO_3)_3$].

2.6 Nutrient Preparation

In any hydrothermal growth process, the physical state of the nutrient is very important. For example in hydrothermally grown quartz, the nutrient ideally is composed of small pieces of natural quartz. For $AlPO_4$ there are many forms of the natural mineral[18] but none of these are in high purity compounds. Therefore the $AlPO_4$ must be synthesized from other compounds. Several things are necessary to have an ideal nutrient for hydrothermal growth. First we must have the correct phase or a transition to it at operating temperature. Next we must have the requisite high purity and solubility. Finally the correct physical form is essential. Preferably the form is a piece of single crystal, a sintered mass, or a glassy solid of the same chemical composition. The main consideration is to prevent any finely divided powders from forming sludge-type masses in the autoclave bottom. This type of behavior impairs easy solubility, mass transport, and loss of correct thermal gradients. Also the surface layer of the caked material is the only thing in contact with the fluid. With the single crystal pieces the fluid can circulate freely throughout the nutrient.

From the Tem-Pres small capsule runs of Section 2.3, it was determined that a satisfactory nutrient can be prepared

from heating a solution of hydrated alumina and H_3PO_4. We scaled up this procedure by using 1.5 inch autoclaves first and then the 3.0 inch autoclaves. The solutions were sealed in silver liners and heated under a gradient of 20-30°C at an increasing temperature and a fixed rate of around 5°C/day over the range of 120-250°C.

The data in Table V refer to some pertinent measurements on two sizes of autoclaves that were used for nutrient preparation. Eventually the process required only the larger autoclave for reasonable yields. It should be noted that the internal silver can liners, which are welded closed, were reusable even though they lose some volume during the opening or closing procedure. Since we are well below critical temperatures and pressures, constant volumes are not necssary to a high degree for simple nutrient preparation.

2.7 Seed Preparation

$AlPO_4$ seed crystals were grown in silica glass tubes by the increasing temperature method.[23] Figure 7 shows a typical seed. A diamond embedded string wire was used to slice the crystals into seed plates. Small holes .050" diameter were drilled in plates for insertion of silver support wire. Cut surfaces were quite smooth. Seeds were ultrasonically cleaned in a soap solution prior to growth. Some seeds also were etched in a H_3PO_4-H_2SO_4 acid mixture. See Section 3.6 for details.

TABLE V

Data for Autoclave Description

Autoclave Size (in)	Internal Cavity Diam. x height (cm)	Cavity Volume (cm^3)	Can Liner Diam. x height (cm)	Can Volume (cm^3)
1.5	3.81 x 38.10	434.4	3.58 x 36.83	370.5
3.0	7.62 x 88.90	4054.	7.34 x 84.46	3572.6

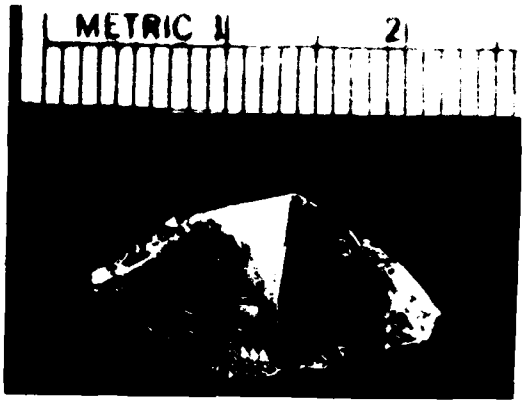


Figure 7. $AlPO_4$ Seed Crystal

2.8 Growth System

2.8.1 Tem-Pres Runs

For small autoclave experimental studies of solubility, phase relations, materials, and crystal growth, Airtron has a Tem-Pres hydrothermal research unit. A photograph of this apparatus is given in Figure 8. There are four complete stations, where each has a furnace and temperature control, a stellite autoclave which has a cavity 0.375 inch diameter x 7 inches long, and a pressure gauge. A hydraulic water pump generates and regulates the pressure of a particular station through an appropriate tubing and valve arrangement.

The Tem-Pres experiments utilize metal capsules constructed of Pt, Au, or Ag tubing as illustrated in Figure 9. The capsules are fabricated by crimping and welding one end in a holding chuck. Such capsules are pictured in Figure 10 before and after loading. The contents are weighed into a capsule; the top is then crimped and welded shut. A sealed capsule is then placed in a reactor, the reactor is filled with H_2O and then closed. The reactor is attached to the pressure system and a preheated furnace is raised into position. Conditions are then arranged for running under the proper temperature, pressure, or thermal gradient. At the end of a particular experiment, the furnace is turned off and the reactor cooled. The capsules are extracted, opened, contents examined, and measurements made.

With respect to the proper choice of metal

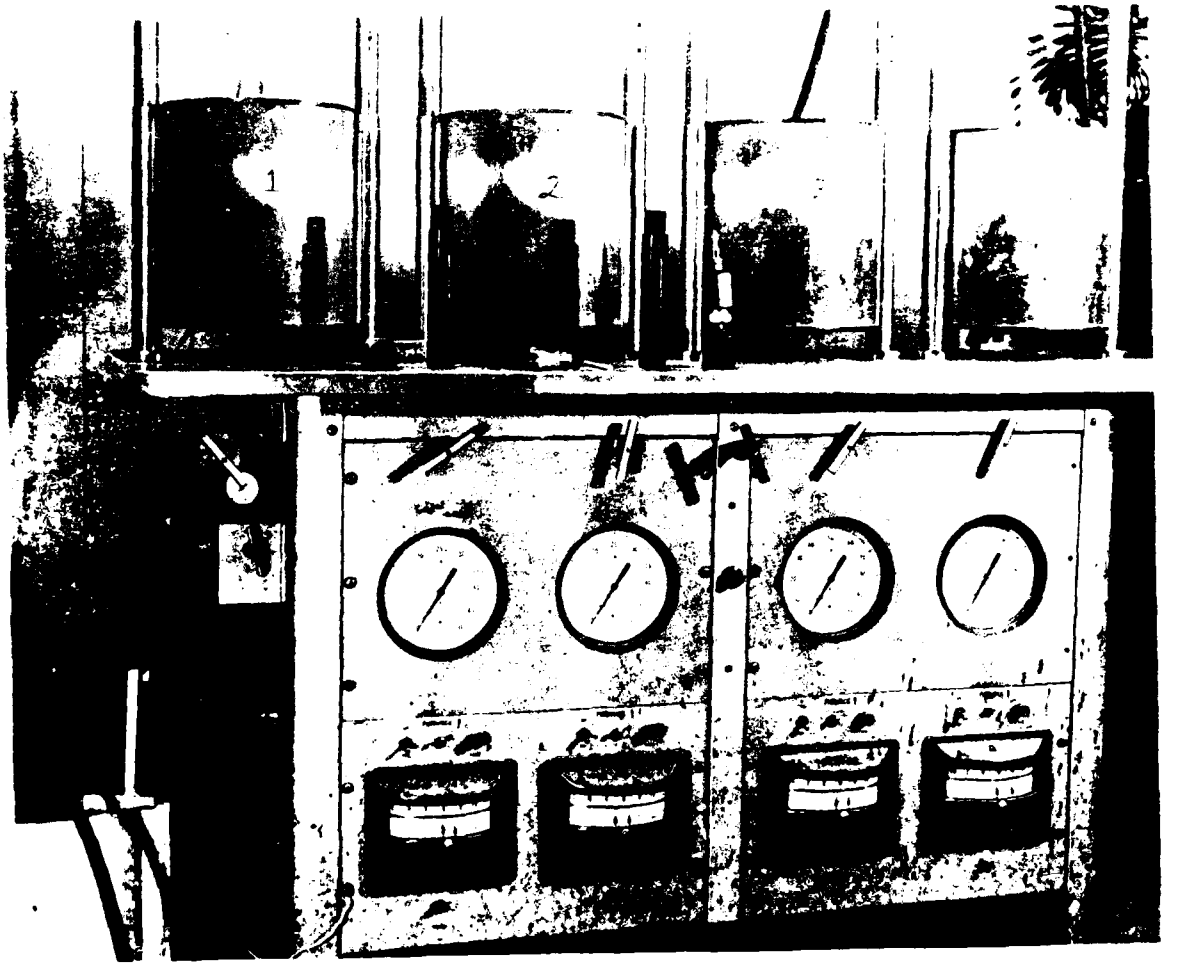


Figure 8 Tem-Pres Hydrothermal Research Unit.

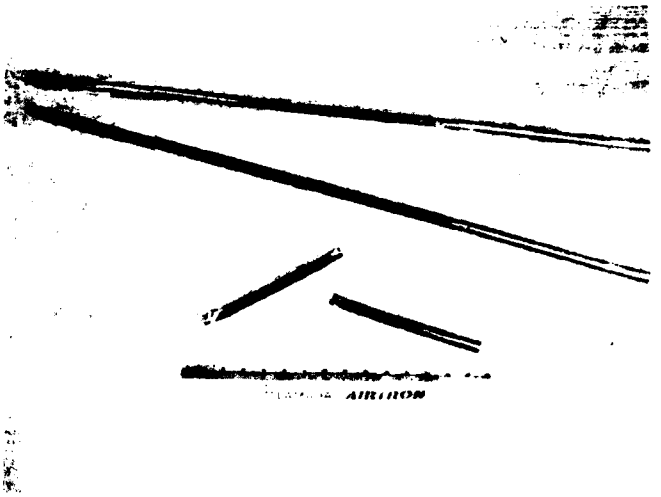


Figure 9 Tubes and Capsules of Silver

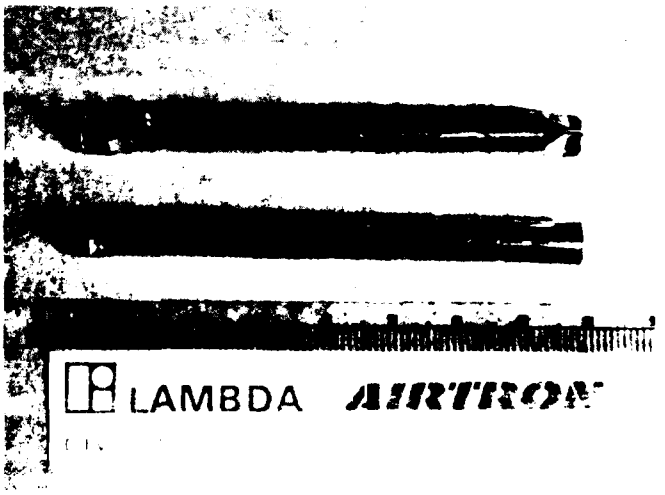


Figure 10 Sealed and Open Silver Capsules

for Tem-Pres runs and can liners for larger autoclaves, it was highly important to try silver because of its lower cost compared to gold or platinum. Therefore our first runs were made to check the corrosion resistance of silver towards 6M H_3PO_4 up to 300°C. In this procedure 85% H_3PO_4 was diluted to 6M and then placed in a silver tube and sealed. The tube was heated to 300°C for 2 weeks and then cooled. After inspection of the inside of the tube, it was found that no leaks, corrosion, or silver transport occurred. Thus we are safe in using silver for can liners.

Other Tem-Pres runs were made with the objective of selecting the best source of hydrated alumina for preparation of $AlPO_4$ nutrient. A typical experiment consisted of dissolving the alumina in H_3PO_4 and then weighing a portion of solution (1-2 cm^3) into a capsule. The silver capsule was sealed and placed in the autoclave under a mean gradient of 20-30°C with the bottom hotter than the top. The starting temperature was 130-140°C and heating was continued for about 25 days to 230°C. At the end of the run the autoclave was cooled rapidly and the capsule then removed.

2.8.2 Autoclaves and Temperature Control System

The 3" O.D. x 1.5" I.D. x 21" long autoclaves (Figure 11) were used for all growth runs and the 6" O.D. x 3" I.D. x 48" long autoclave (Figure 12) was used for the most part in the nutrient preparation. The 1.5" I.D. autoclaves were composed of Unitemp-41 which are rated at maximum conditions of 650°C, 30,000 psi. These conditions are well in excess of the

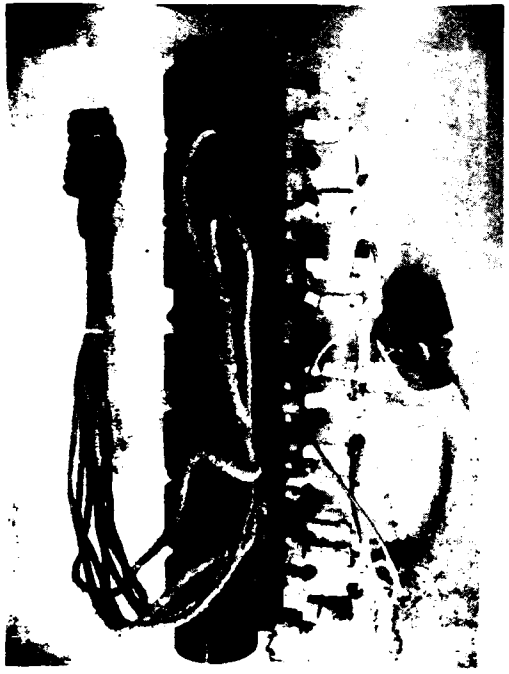


Figure 11 1.5 Inch Diameter Autoclave with Bandheaters and Thermocouples

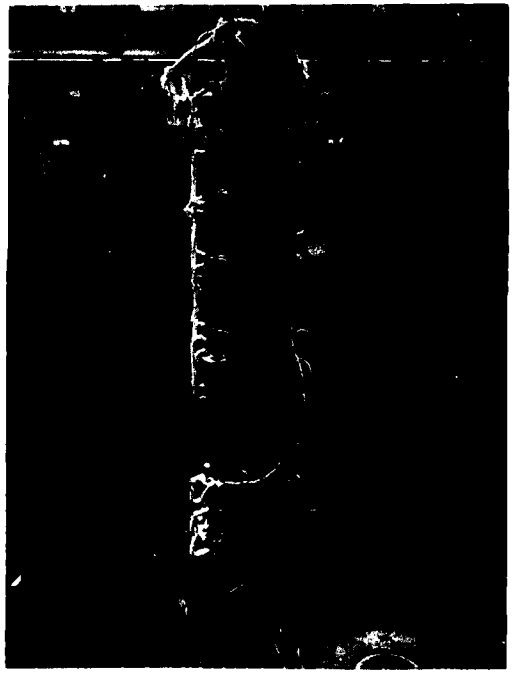


Figure 12 3.0 Inch Diameter Autoclave with Bandheaters and Thermocouples

the actual growth parameters for $AlPO_4$. The large autoclave was made of A-286 which was also satisfactory for growth. All the vessels used the "modified Bridgman" seal. Table 5 gives the volumes of the appropriate autoclave as well as some liner data.

The small autoclaves are equipped with resistance bandheaters arranged on the autoclave to allow independent temperature control of three separate zones. Power is distributed to the heater by a West JT-3 temperature controller in conjunction with three manually adjustable potentiometers, one to each zone. (Figure 13)

The larger autoclave was also equipped by band heaters. The heaters are arranged into four zones along the length of the vessel. Power is distributed and controlled by a West JSBG-3R program controller with the S-92 option, and a West-2R-546 differential controller. (Figure 14) This equipment allows us to program temperatures up and down with a fixed gradient between the top two and the bottom two zones. Furthermore gradients within the bottom and top zones can be controlled by Variacs wired into the system.

2.8.3 Autoclave Liners

A steel autoclave is usually corroded to some degree when acid or basic solutions are in contact with metal. For quartz it is fortunate that NaOH forms a rather inert layer on the surface called acmite of composition $Na_2O \cdot Fe_2O_3 4SiO_2$. Therefore quartz can be grown in unlined autoclaves with no

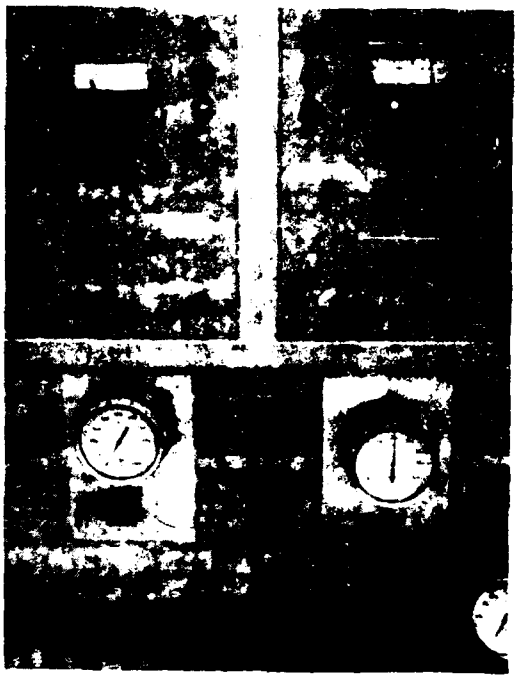


Figure 13 Temp. Controls for 1.5 Inch Autoclaves

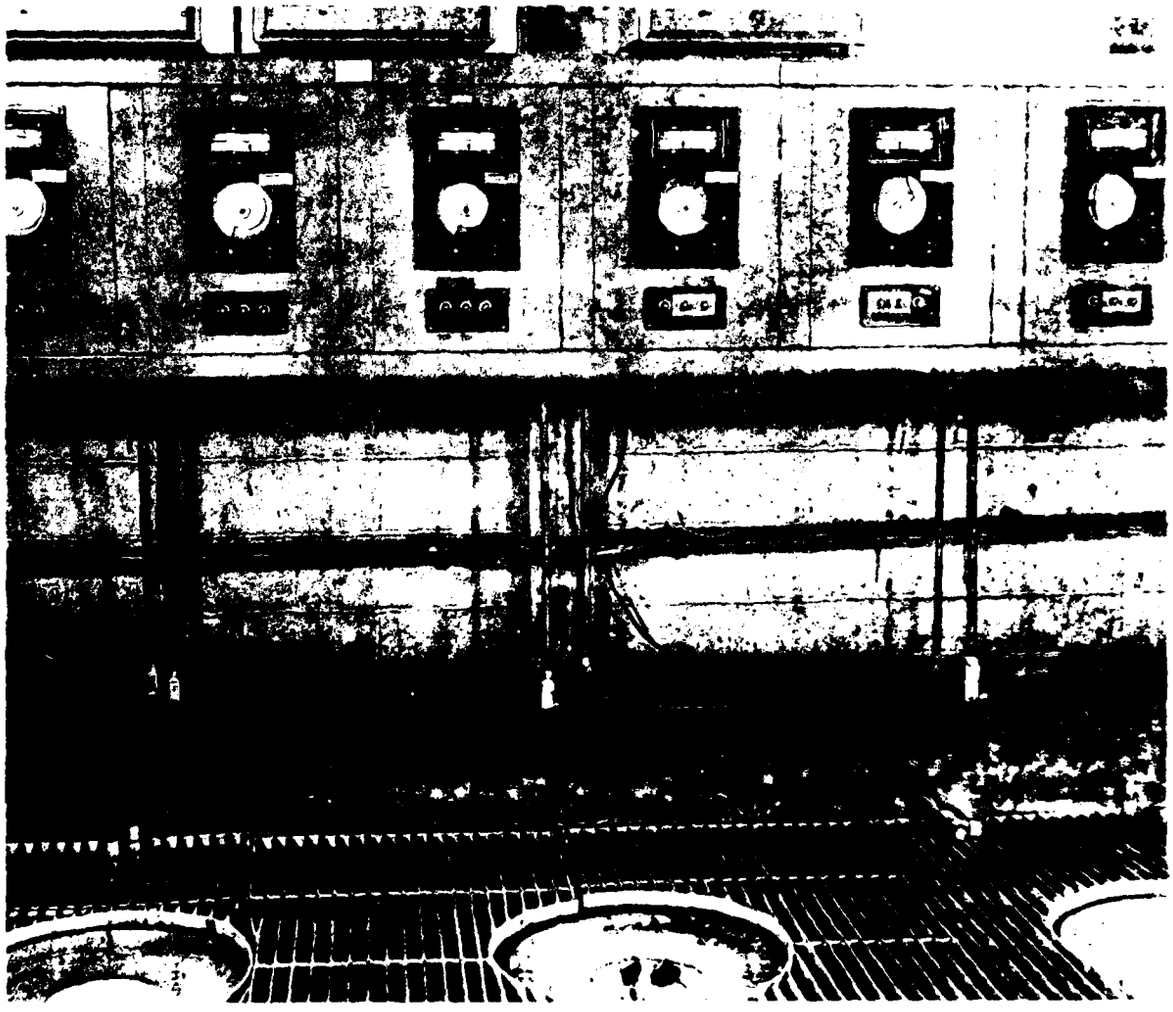


Figure 14 Temperature Controllers and Programmers for the 3" I.D. Autoclaves.

damage. For all other materials some form of inert barrier must be used to contain the solution and prevent damage to the autoclave during use. The type of protection required depends on the solvent, grown material and operating conditions.

For $AlPO_4$ growth it is necessary to grow from an acid solution high in PO_4^{3-} and low in pH. Fairly high levels of H_3PO_4 are quite corrosive to most material particularly as the temperature is raised above 150°C. The normal materials which can be used are glass, Teflon, graphite, vitreous carbon and metals such as silver, gold, or platinum. At Airtron we have determined that silver is useful in PO_4^{3-} solutions up to about 450°C if the pH is not too low. Platinum and gold are much more expensive but all the metals can be reclaimed for value. Graphite or other carbon materials are difficult to seal. Teflon can be sealed by gaskets but does start to soften around 300°C and creep severely. Glass is satisfactory but sealing problems can arise and fractures are common. If complicated seed holders, ladders, baffles, etc. are to be used, the overall best working material is silver. This metal can be welded easily and Airtron has worked with autoclave liners from 1 inch up to 8 inches in diameter and 10 ft. high. Some of the theory and practical use of large noble metal cans can be found in an early paper of Airtron work.[18]

Silver tubes were ordered from a commercial supplier. These tubes are seamless and cut to a specified length. Fine silver discs are used for the bottom and are seam

welded to the tube. (See Figure 15) The top closure on the cap has a vent pipe welded to it. This pipe is used for filling the can with water or solution. Finally a baffle is welded to the top of the seed ladder which is positioned in the bottom of the liner. The nutrient basket is attached to the lid by means of a hook. When all the seeds and nutrient are arranged in the tube, the lid is welded. The solution is then added through the vent tube and welded shut. Figure 16 shows the components of a liner used in an early run. The nutrient basket was later replaced with one shown in Figure 17. These baskets were fabricated by hammer welding either 40 or 80 mesh screen over an appropriate size mandrel.

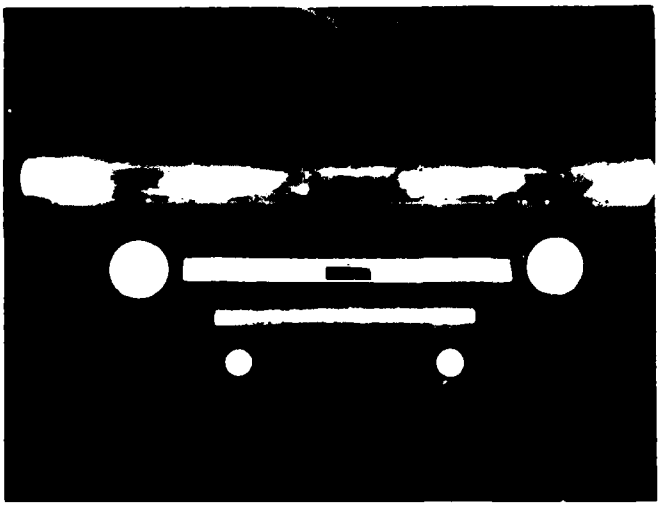


Figure 15 Silver liners for 1.5 Inch I.D. and 3 inch I.D. autoclaves.

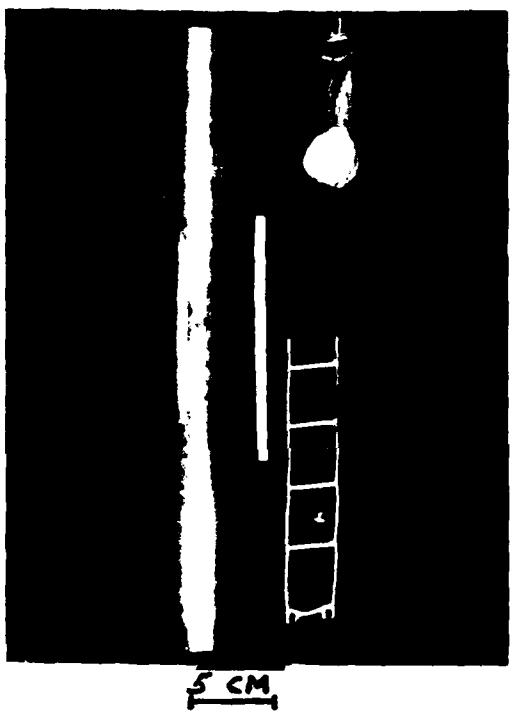


Figure 16 1.5 Inch Silver Liner, Nutrient Basket and Seed Ladder.

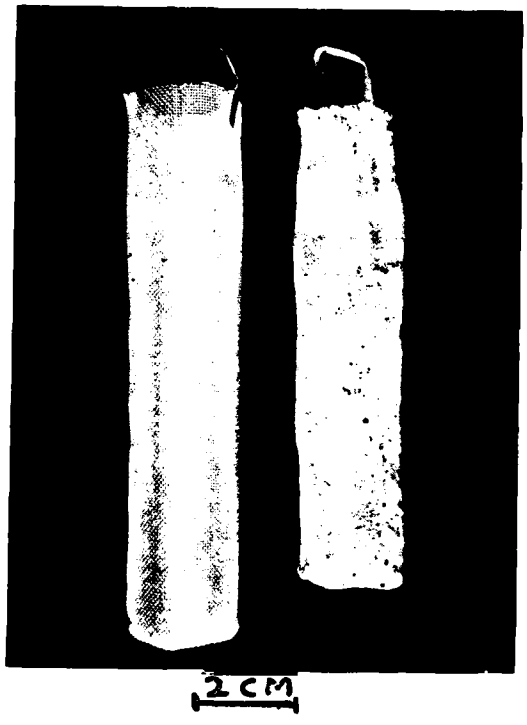


Figure 17 Nutrient Baskets: Left - 40 mesh, Right - 80 mesh.

3.0 Results

3.1 Nutrient Yield

The clear saturated solution of $Al(OH)_3$ in 6M H_3PO_4 was sealed in silver tubes and crystallized over several weeks by gradually increasing the temperature in a range of 130-200°C. Figure 18 shows a typical result. Small euhedral crystals in the 1-4 mm range were produced. The material was checked by x-ray diffraction and identified as α-$AlPO_4$. The particle size was suitable for an ideal nutrient. Nutrient preparation in the large 3 inch I.D. liners yielded about 950 gm which was sufficient for many growth runs.

3.2 Seed Growth of $AlPO_4$

The fundamental change in the growth of α-$AlPO_4$ is how one deals with the retrograde solubility. Stanley[2] proposed and perfected two methods. Earlier work utilized a repetitive cycle wherein the temperature was held constant at 160°C and fresh solution was added every two days to the system. While this procedure grew crystals, one can see that it easily leads to much work, high nucleation, poor quality, twins, inclusions, lack of control, and poor material. The second method was a single cycle growth where the autoclave remained sealed and temperature was raised from 133° to 155° over a period of 45 days. This procedure is analogous to the one described by other workers[3] except that the latter crystallization temperature was about 300-315°C. For reasons of autoclave operation, the possibility of high quality, and

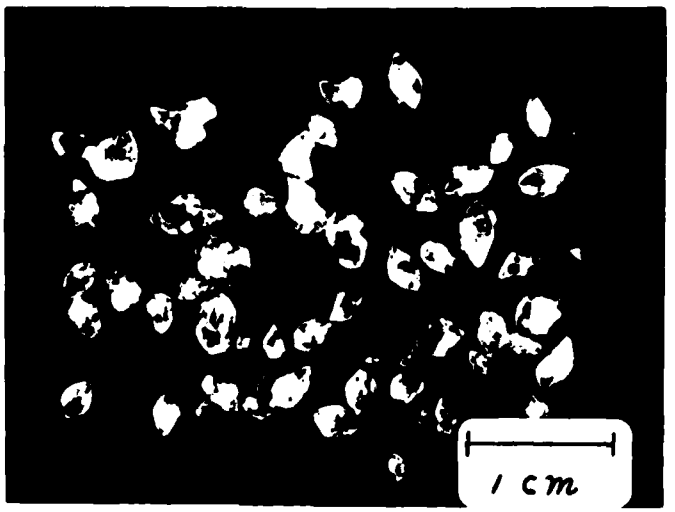


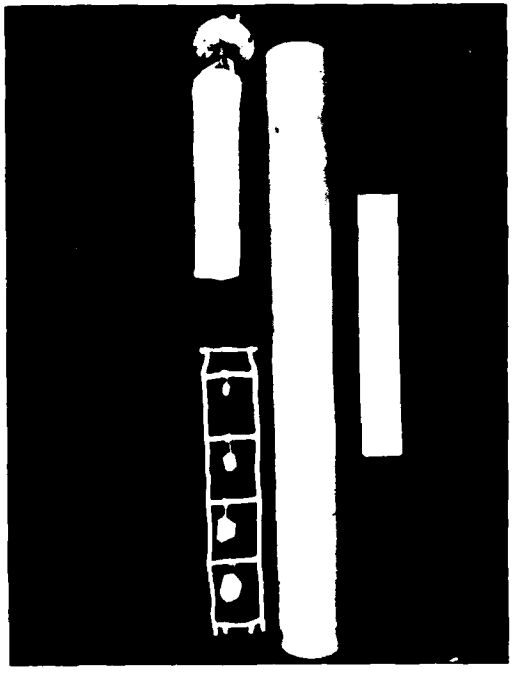
Figure 18 Close up of $AlPO_4$ Crystals

method. First we notice that in most solution growth, the control of temperature is highly important and that free crystallization by cooling or heating is bound to lead to some random nucleation, growth, and general loss of control. Thus any procedures where nutrient and seed temperatures are held rather constant is more likely to give reproducible results, better growth conditions and excellent quality.

Most of the seeded growth runs had the arrangement shown in Figure 19. A silver gauze nutrient basket was suspended from the cover at a height to be submerged in the 6M H_3PO_4 solution when 80% internal fill was used. The seeds were hung on a silver wire rack near the bottom of the liner. A gradient ranged between 8-30°C with the bottom temperature hotter than the top. A rapid heating rate was used to reduce seed dissolution. The convection caused by the thermal gradient continually transported $AlPO_4$ from the cold to the hot region (or where the solubility of $AlPO_4$ is higher to where it is lower). By placing the nutrient basket in the solution during heat-up, the nutrient will dissolve in the top, cooler portion of the solution and is less likely to dissolve the seeds.

3.3 Thermal Gradients

The amount of nutrient transport in a growth run is mainly controlled by the thermal gradient along the length of the liner. A large amount of nutrient transport however, is not always desirable because of the rapid growth rates which can cause poor quality. The values were 10-15°C which produced growth



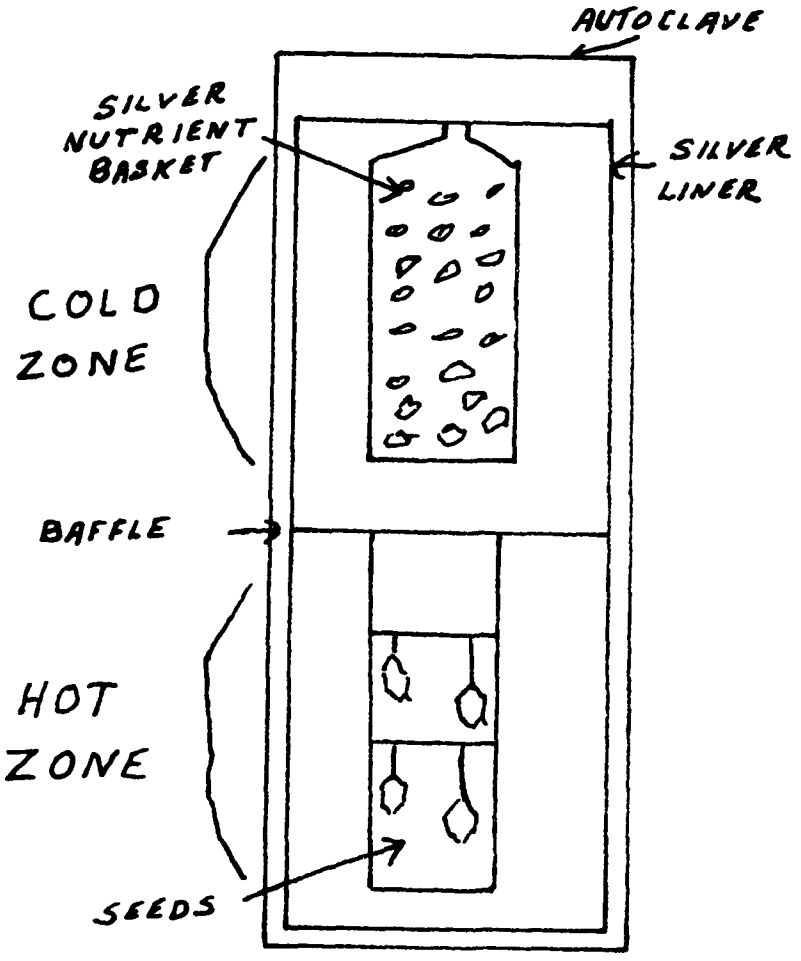


Figure 19 Typical Seeded $AlPO_4$ Growth Run

rates ranging from 10-30 mils/day. A low gradient also produced a better seed growth to spontaneous nucleation ratio. In most hydrothermal growth, as the temperature increases the solubility does also and the convection currents transport material for growth on the seeds. With retrograde solubility, high temperatures lower the solubility but the convection currents are still comparatively rapid. If the temperature is too low, the solubility will be high, but the convection currents may be quite small and not transport sufficient nutrient.

Two growth runs were completed where a negative thermal gradient was used. This type of arrangement had the colder saturated solution around the nutrient at the bottom of the liner with the seeds in the hotter upper portion. Convective transport of the nutrient would be quite low and in both cases the seeds were dissolved. The negative gradient method was not used for any other runs.

3.4 Baffle Design

For seeded growth of $AlPO_4$, a baffle was designed to reduce any irregular convection currents and provide a more isothermal chamber in the seed region. The per cent free opening of the baffle was 20% which distributed growth on the various seed crystals uniformly. With a smaller per cent free opening the bottom seeds grew larger and with a larger opening the top seeds were larger.

3.5 Chemical Analyses

Emission spectrographic analyses (Table VI) were obtained from samples of the starting materials, nutrient and single crystal. Sample #1 was the starting chemical for most of the single crystal growth runs and was very high in sodium. The nutrient (#2) which was transported and recrystallized in the autoclaves, did not detect any sodium. As expected, the process of crystallization purified the material. Sample #3 was the single crystal grown from this nutrient. None of the iron, magnesium, sodium or silicon originally in the nutrient were incorporated into the final crystal. The titanium present can not be explained. Sample #4 was a higher purity starting material. The nutrient prepared was similar in purity to the nutrient obtained from the hydrated alumina. Several of the samples had quantities of boron present which resulted from grinding in a boron carbide mortar and pestle. The two starting chemicals (#1 and 4) were not ground and had no boron detected. The two nutrient samples also had unhomogeneous silver which can be attributed to sawing the end off the silver liner to remove the nutrient. Small amounts of silver can unavoidably get mixed with the $AlPO_4$.

3.6 Chemical Etching

The quality of seed plates and crystals were studied by etching in a solution of equal volumes of sulfuric and phosphoric acids for 1 minute at 140°C. Figure 20 shows the hexagonal shaped etch figures observed on a (0001) seed plate.

Table VI

Spectrographic Analyses

SAMPLE	#1	#2	#3	#4	#5
Silver	--	*1	0.001%	--	*1
Aluminum	High	High	High	High	High
Boron	--	0.005%	0.001%	--	0.01%
Iron	0.002%	0.001%	--	0.001%	0.001%
Gallium	0.002%	0.002%	0.002%	--	--
Magnesium	--	0.001%	--	--	0.001%
Sodium	0.05%	--	--	--	--
Silicon	0.001%	0.001%	--	0.001%	0.002%
Titanium	--	--	0.003%	--	0.001%
Phosphorous	--	Present	Present	--	Present

High 10-100% Medium 1-10% Low 0.1-1% Trace less than 0.1%

Note: Other Elements Not Detected

*1 - Silver Unhomogeneous - Range Trace - Low to Low-Medium

Sample No.

1	Alcoa $Al(OH)_3$
2	Nutrient prepared from Sample 1
3	Single crystal of $AlPO_4$
4	Aluminum isopropylate
5	Nutrient prepared from Sample 4

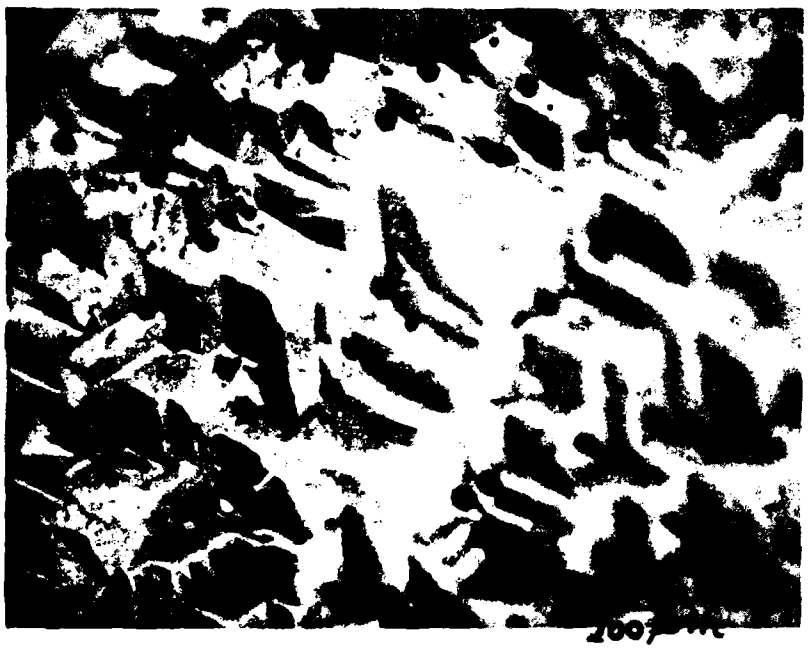


Figure 20 Hexagonal Etch Figures in $AlPO_4$ Crystal.

3.7 Crystal Growth Rates

Growth rates for seeded $AlPO_4$ using the constant temperature method with a thermal gradient can be varied depending on such parameters as growth temperature, gradient, nutrient basket mesh size, seed orientation and baffle design. A growth temperature of about 175°C with a gradient of 10°C produced rates ranging from 10-18 mils/day which were the largest. By changing the nutrient basket from an 80 to 40 mesh, under the same growth parameters, the rate increased to 23-25 mils/day. The amount of nutrient dissolved increased with the larger mesh size and more was transported which increased the rates. The amount of spontaneous nucleation in each case was about the same. The above rates were for (0001) seed plates. A seed perpendicular to a (0001) plate produced only 4 mils/day of growth. The baffle was designed to create an isothermal chamber in the seed region but the per cent free opening distributed growth in that region and altered growth rates.

The growth rates for the constant temperature method were quite satisfactory for short duration runs of about a week but decreased significantly for long runs. The increasing temperature technique maintained the rate for the entire run to produce good size crystals. The rates usually ranged from 22-32 mils/day although one run reached as high as 46 mils/day. The temperature increase was approximately 5°C/day.

Due to crevice flaws which were present with (0001) seed plates, a different orientation was also used. Rhombohedral seeds, which are natural faces for $AlPO_4$, produced growth rates of 2-3.6 mils/day. These rates are similar to 6 mils/day reported by Croxall (1979) et al.[20]

3.8 Crystal Quality

New growth of $AlPO_4$ for the most part was clear and of fair quality. Two problems with quality however, were observed. The crystals had what appeared to be high angle grain boundaries as seen in Figure 21 which were traced to the original seed plate. It was quite evident that the quality of the starting seed determined the overall quality of the grown crystals. The size of the "grains" varied from run to run but were present in almost every instance. A second feature observed was deep pits or crevices found on the (0001) face of the crystals (Figure 22). It appeared that perhaps the growing crystal was nutrient "starved". The small mesh size (80 mesh) of the nutrient basket was thought to be restricting dissolution of the $AlPO_4$ nutrient. A 40 mesh basket was fabricated, which appreciably increased growth rates, but the crevices remained. These deep crevices did not appear to originate from the seed and therefore did not result from an improperly prepared seed surface. This surface was etched before growth as described in Section 3.6 to remove any possible saw damage. The necessity of acid etch prior to growth was

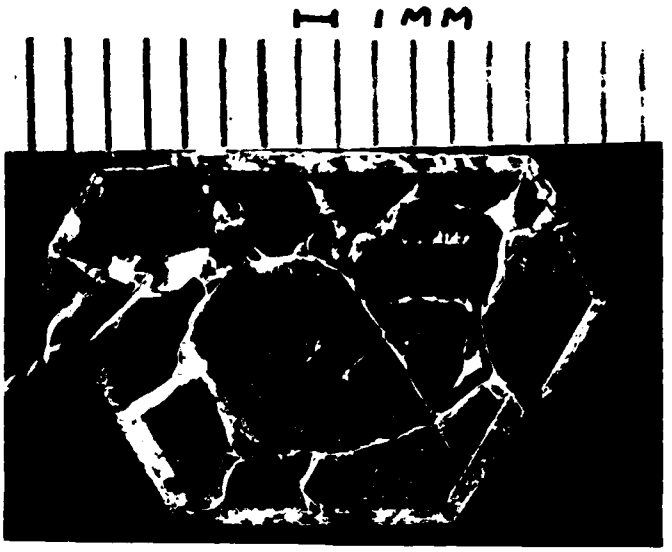


Figure 21 Grain Boundaries Observed in $AlPO_4$ Crystal.

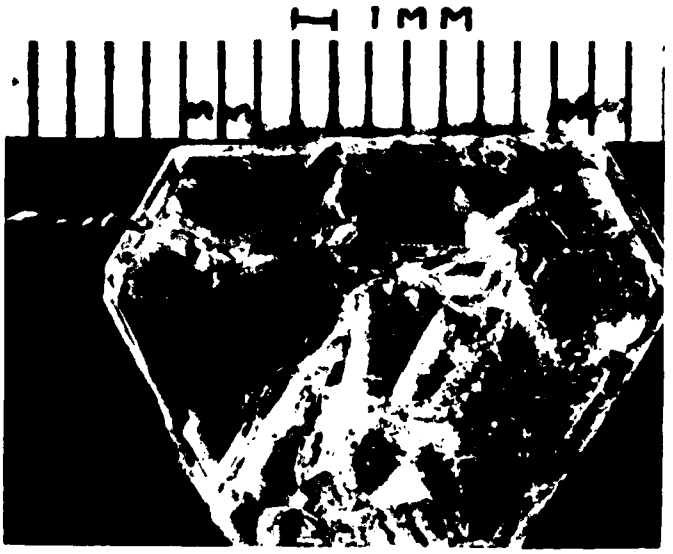


Figure 22 Deep Pits or Crevices Observed in $AlPO_4$ Crystal.

unclear, because as already described, some dissolution of the seeds occurred during heat-up. No visible difference was evident between etched and unetched seeds. Other workers have reported[20] the crevice flaws when the overgrowth reached a thickness of about 2 mm on seed plates cut parallel to the basal plane. They also found more satisfactory growth using rhombohedral seed plates, however growth rates were much slower.

Crystals grown by the constant temperature technique and those grown by the increasing temperature method usually had high angle grain boundaries and crevice flaws. A particular crystal looked quite clear. The seed plate was indistinguishable from the overgrowth. By immersing the crystal in naptha, reflections were eliminated and the very transparent internal quality could be observed. As usual, deep crevice flaws were present on the surface.

3.9 Growth Run Examples

All the seeded aluminum phosphate growth run data are listed in Table VII, including comments. Growth rate calculations are for both sides of the seed crystal. Thickness rates were measured in the [0001] direction except where otherwise indicated. Runs 7-26, 31 were grown with the constant temperature method while 27-30, 32, 33 used the increasing temperature technique. Figure 23 shows some of the larger crystals produced.

4.0 DISCUSSION

The single crystal growth of α-$AlPO_4$ by the hydrothermal method encountered numerous difficulties such as: poor quality

Table VII

DATA FOR $ALPO_4$ SEEDED GROWTH RUNS [1]

Run Number		7	8	9	10	11
Run duration (days)		8	7	7	8	17
T. of liner (°C)	Top	235	238	268	215	205
	Bottom	288	250	277	227	215
	ΔT	53	10-12	9	10-13	10
Pressure (psi)		2000	750	1000	500	250
Nut. dissolved (gm/day)		5.4	5.6	1.9	3.6	1.89
SN (gm/day)		3.7	3.0	1.0	78	.16
SN/Nut. dissolved		.68	.54	.53	.22	.8
Wt. gain (gm)	1					
	2	.1521	.2998		.328	.3673
	3					
	4	.1259	.2660		.327	1.069
Total wt. gain/day (gm)		.0348	.0808		.0819	.0845
% wt. gain/day	1					
	2	0.7	12		7.5	2.4
	3	0.4	7.4		8.8	10.4
	4					
Growth Rate Thickness (mils/day)	1					
	2					
	3					
	4					
Length (Width)	1					
	2					
	3					
	4					
Basket Mesh		[illegible]	[illegible]	80	80	80
Comments:		[illegible]		Run terminated		1st baffle run 22% free opening

Table VII (Continued)

DATA FOR $ALPO_4$ SEEDED GROWTH RUNS [1].

Run Number		12	13	14	15	16
Run duration (days)		7.5	7.5	7.5	7.0	7.5
T. of liner (°C) Top		242	191	164	161	152
Bottom		252	193	175	190	161
ΔT		10	12	10-12	29	9
Pressure (psi)		500	150	75	100	50
Nut. dissolved (gm/day)		3.8	3.4	3.6	4.5	4.91
SN (gm/day)		.8	.13	.07	.21	.03
SN/Nut. dissolved		.22	.04	.02	.05	.005
Wt. gain (gm)	1	-.0490		.7391	.0957	.0144
	2	.0055	.3408	.4144	.1511	.0074
	3	.0058	.7323	.8594	.3244	.0635
	4	.0490	.6739	.7497	.3030	.0375
Total wt. gain/day (gm)		.007	.234	.366	.125	.016
% wt. gain/day	1			18.1	6.8	.6
	2		12.8	7.7	1.9	
	3		17.3	8.6	2.2	3.0
	4		6.0	4.6	1.5	.2
Growth Rate Thickness (mils/day)	1			22.5	6.1	1.5
	2		11.6	17.5	5.6	1.2
	3		14.3	18.4	6.9	1.5
	4		12.0	10.3	8.3	0
Length (Width)	1			0.5 (-.8)	1.6	
	2		2.3 (1.6)	.3 (1.3)	1.3 (1.6)	
	3		1.2 (1.2	1.3 (-.8)	1.6 (1.6)	
	4		.5 (1.6)	1.7 (12.9)	.6 (-5.4)	
Basket Mesh		80	80	80	80	80
Comments:		Very little growth	Good growth	Large growth rate	Smaller growth rate	Very low temp., little growth

Table VII (Continued)

DATA FOR $ALPO_4$ SEEDED GROWTH RUNS [1].

Run Number		17	18	19	20	21
Run duration (days)		20.5	7.0	7.0	7.0	7.0
T. of liner (°C)	Top	163	177	192	164	167
	Bottom	175	165	160	179	176
	ΔT	12	-12	-32	15	9
Pressure (psi)		100	100	175	125	50
Nut. dissolved (gm/day)		1.81				4.2
SN (gm/day)		.46				.39
SN/Nut. dissolved		.26				.09
Wt. gain (gm)	1	1.4833			.5426	.742
	2	1.8235			.2154	
	3	.4610			.5322	.8414
	4	1.5856			.6996	.7768
Total wt. gain/day (gm)		.26			.28	.337
% wt. gain/day	1	19.4			19.6	32
	2	20.6			19.5	
	3	10.1			63.2	32.5
	4	19.0			26.5	29.2
Growth Rate Thickness (mils/day)	1	10.3				14.9
	2	11.0				
	3	7.5				15.1
	4	10.4				15.0
Length (Width)	1	7 (1.3)				2.5 (2)
	2	.9 (1.6)				
	3	.8 (1.4)				17 (2)
	4	1.4 (1.4)				2.5
Basket Mesh		80	80	80	40	80
Comments:		Good growth rate	Negative gradient dissolved all seeds in upper part of liner. Nutrient in the bottom.			

SEEDS DISSOLVED

POLYCRYSTALLINE GROWTH

Table VII (Continued)

DATA FOR $ALPO_4$ SEEDED GROWTH RUNS [1].

Run Number		22	23	24	25	26
Run duration (days)		7.0	7.5	7	7	10
T. of liner (°C)	Top	166	176	168	165	163
	Bottom	174	186	178	175	173
	ΔT	8	10	10	10	10
Pressure (psi)		50	125	125	100	100
Nut. dissolved (gm/day)		6.3	5.5	6.31	3.62	2.75
SN (gm/day)		.29	.35	.29	0	0
SN/Nut. dissolved		.05	.06	.04	0	0
Wt. gain (gm)	1	.742	.5996	1.1101	-.0988	.0765
	2		.6601	.8015	-.0536	.0327
	3	1.2134	.5384	.250	-.0428	.0575
	4	1.3941	.3672	.8618	-.01346	.0605
Total wt. gain/day (gm)		.479	.289	3.02		.02
% wt. gain/day	1	35.4	26.2	34.9		2.2
	2		5.3	34.7		2.1
	3	49.3	21.1	10.8		0.5
	4	74.3	18.5	28.2		3.1
Growth Rate Thickness (mils/day)	1	23.0	10.4	18.5		1.4
	2		11.7	20.2		1.6
	3	24.3	12.5	4.1		1.7
	4	24.7	15.6	22.0		1.7
Length (Width)	1	3.7 (3.4)	0.8	2.3 (2.7)		
	2		1.1 (1.9)	1.8 (2.7)		
	3	3.4 (4.6)	1.3 (2.0)	3.2 (19.4)		
	4	4.1 (3.7)	2.0 (2.2)	3.7 (2.1)		
Basket Mesh		40	40	40	80	80
Comments		Increase in growth rate with larger mesh basket	Good wt. gain perpendicular to [illegible]	Good wt. gain		

DECREASED WEIGHT

DECREASED LENGTH & WIDTH

Table VII (Continued)

DATA FOR $AlPO_4$ SEEDED GROWTH RUNS [1].

Run Number		27	28	29	30	31
Run duration (days)		13.5	17.5	14.5	13.0	14.5
T. of liner (°C) Top		141-192	129-194	130-186	112-194	473
Bottom		148-202	135-210	133-200	124-207	455
ΔT		9	14	14	13	22
Pressure (psi)		60-195	25-250	25-200	25-200	21-250
Nut. dissolved (gm/day)		3.44	2.9	3.3	3.62	
SN (gm/day)		.26	.52	.60	.71	
SN/Nut. dissolved		.08	.18	.18	.19	
Wt. gain (gm)	1	2.0558	1.5924	1.9532	1.9153	
	2	2.9157	.3820	3.2462	1.2548	
	3	2.4706	3.706	3.3142	2.1370	
	4	2.5169	3.4894	2.8834	1.1732	
Total wt. gain/day (gm)		.74	.5	.79	.49	
% wt. gain/day	1	16.8	31.8	50.5	50.89	
	2	13.8	14.1	74.4	34.3	
	3	17.0	30.3	63.8	43.4	
	4	16.1	23.7	76.4	46.7	
Growth Rate Thickness (mils/day)	1	22.3	28.3	42.2	30.2	
	2	22.8	20.4	45.2	32.9	
	3	24.3	26.9	46.0	31.8	
	4	22.9	27.3	44.6	31.9	
Length (Width)	1	3.2 (11.0)	2.7 (2.3)	3.7 (4.8)	1.6 (4.2)	
	2	2.8 (10.2)	1.4 (.8)	4.6 (6.7)	1.5 (3.6)	
	3	3.7 (13.0)	4.2 (3.5)	5.5 (6.1)	4.9 (2.8)	
	4	4.4 (15.9)	4.1 (3.8)	4.4 (4.4)	3.0 (2.4)	
Basket Mesh		40	40	40	40	8
Comments		Increased temperature variation			9 M solution. Significant amount of transmission	

SEEDS DISSOLVED

Table VII (Continued)

DATA FOR $ALPO_4$ SEEDED GROWTH RUNS[1].

Run Number		32	33	34
Run duration (days)		15	12	21
T. of liner (°C) Top		123-303	130-199	137-175
Bottom		133-213	140-210	150-192
ΔT		10	10	13
Pressure (psi)		0-250	25-200	45-150
Nut. dissolved (gm/day)		2.8	3.4	1.6
SN (gm/day)		.03	.11	.2
SN/Nut. dissolved		.012	.036	.13
Wt. gain (gm)	1	3.9726	3.0391	.6426
	2	3.1514	3.5620	.7310
	3	3.8784	4.0764	.4849
	4	3.7303	3.8397	1.1883
Total wt. gain/day (gm)		0.982	1.210	0.145
% wt. gain/day	1	36.3	35.0	13.1
	2	48.9	36.3	6.8
	3	42.5	31.1	6.4
	4	39.8	34.8	20.5
Growth Rate Thickness (mils/day)	1	30.1	28.9	3
	2	31.4	30.1	2
	3	32.1	27.9	4
	4	32.3	29.7	3.6
Length (Width)	1	2.2 (2.7)	3.0 (2.8)	---
	2	2.7 (2.2)	2.2 (2.7)	---
	3	4.4 (2.7)	3.9 (3.1)	---
	4	3.9 (5.2	3.3 (3.1)	---
Basket Mesh		40	40	40
Comments:				Rhombohedral seed plates

1. a) 6 M solution for all runs except #31
   b) 80% internal fill
   c) All seeds are (0001) plates unless specified
   d) Growth rates are for both sides of the crystals

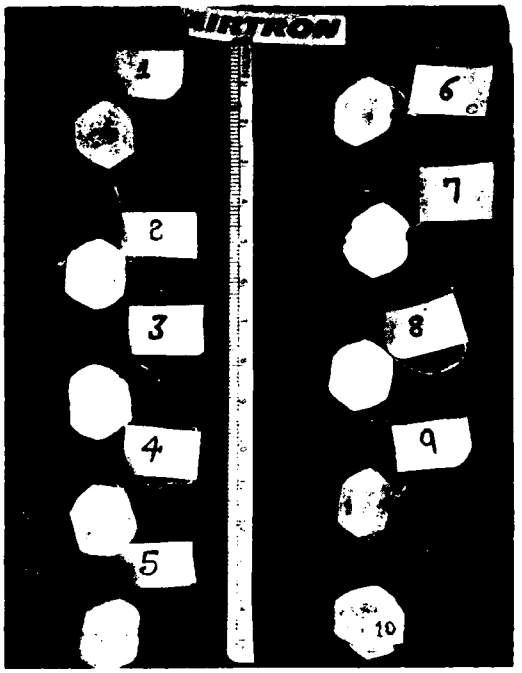


Figure 23 $AlPO_4$ Crystal Grown by the Increasing Temperature Method.

starting materials (purity and stoichiometry), nutrient particle size, inert liner for acid containment, retrograde solubility, unsustained growth rates, and persistent quality defects.

Pure $AlPO_4$ from a commercial vendor has not been available. Most materials are hydrated $AlPO_4$ or entirely different phases with various stoichiometries. A suitable method (Section 2.3) has been developed for the production of $AlPO_4$ which also meets the particle size requirements for a satisfactory nutrient.

Inert silver liners were designed to contain the corrosive phosphoric acid solution necessary to dissolve and transport the aluminum phosphate. These liners proved quite successful provided certain welding precautions were observed.

Aluminum phosphate is one of the few compounds that has retrograde solubility which necessitated new techniques. A nutrient basket was fabricated from silver mesh to contain the $AlPO_4$ in the upper portion of the liner. The bottom of the liner could then be hotter than the top to fully utilize the convection currents which are very important for satisfactory transport and growth. The usual method of nutrient at the liner bottom with a negative gradient was unsatisfactory.

The constant temperature method with a gradient produced good growth rates for short duration runs. As the run time was extended to 2-3 weeks, the rates unexpectedly decreased. At the constant temperature with a nutrient supply, the transport and growth of $AlPO_4$, driven by the thermal gradient

should maintain a reasonably stable growth rate. This rate should be sustained until the nutrient supply is exhausted or some other factor such as the basket mesh or baffle is blocked. Nothing was observed after a run that could explain the rate decrease.

As already discussed in Section 3.8, certain quality problems persisted. The best quality seeds available were used as well as various seed orientations and starting materials purity.

5.0 CONCLUSIONS

Large size $AlPO_4$ single crystals have been grown by other workers[2] using the multiple cycle technique where the seeds are repeatedly used in runs to gradually increase size. This type of successive overgrowth caused quality problems at the seed interface. The best quality hydrothermal crystals are produced at constant temperatures with a nutrient source. Therefore, this program was initiated using the constant temperature method. Most of the problems of retrograde solubility, containment of strong acid solutions and nutrient preparation were solved. Growth rates were for the most part suitable although there was a tendency for the rate to decrease during long duration runs. Problems with crystal quality on (0001) seed plates were prominent so other orientations were studied. Rates for the other directions were very slow however.

The increasing temperature technique was also studied to

determine the effects on quality. Basically the growth run is identical to the isothermal temperature method except the solution is rapidly heated to 150°C and then slowly heated at 1.5 to 5°C/day to 200°C. The average growth rates were large which yielded crystals considerably larger than the first technique for an equivalent length of time. The basic quality problems of crevice flaws remained. The best quality seeds available were used for growth. Usually the quality of overgrowth is reflected by the seed quality. The preparation of the seed surface was also studied to observe the effects on quality. Seed etching prior to growth did not appear to change the quality of the final crystals.

The relationship between starting materials purity and crystal quality was examined by spectroscopic analysis. The process of crystallization purified the final crystals as expected. For example, the initial materials had high levels of sodium but was not detected in the single crystal. The crystallization process is rather selective in purification in that the gallium was present at the same levels in the starting materials, the nutrient, and the single crystal. The possibility remains however, that an impurity may not be incorporated into the crystals, but still affect the growth process.

The quality problem of $AlPO_4$ does not appear to have a simple solution. All of the items discussed above have not solved the difficulties encountered. A more detailed study

is necessary to ascertain the exact nature of the quality defects and their relationship to the growth process.

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